8/17/12

Review of: Pavillion Phase V Summary Spreadsheet *(Pavillion Apr2012 QA Summary v2.3 8_13-2012.xlsx)*

1. QC Flags: Replace the QC Flags table with the one included in the QAPP Addendum.

2. Anions and Ammonia: Bromide: The MDL should read 0.129, not 0.059. Make changes in all affected data and apply the U flag.

3. Organic Acids: Lactate: Results for four samples are "<0.0009." One too many decimal places. Replace with "<0.009."

4. sVOC:

- Is the analyte tri-(2-butoxyethyl) phosphate the same as 2-butoxyethanol phosphate as reported by region 8?
- EPAMW01-0412-7: Result for R-(+)-Limonene should read "1.98", not "<1.00"
- EPAMW02-0412-1: Benzoic Acid flagged J7; not sure why as the field dup taken on same day was ok
    - The J2 flags should be replaced with the following as indicated for matrix spike recoveries or hi RPD for MS/MSDs:
        1,3-dimethyladamantane, K2
        2,4-dimethylphenol, K1
        2-Butoxyethanol, K1
        4-chloroaniline, K2
        4-nitroanilne, K2
        Adamantane, K2
        Benzo(a)anthracene, K2
        Benzyl alcohol, K2
        Hexachlorocyclopentadiene, J6
        Hexachlorothene, J6
        N-nitroso-n-propylamine, J6
        Phenol, K2
        3-nitroaniline, K2
        Bis(2-ethylhexyl) adipate, K1
- Low LCS (Method Blank spike) in batch 1200240 for both 1,3-dimethyladamantane and adamantane, flag K2, and for hexachlorocyclopentadiene, flag J6 (hi RPD for MS/MSD), samples:
    - PGDW50-0412
    - EPAMW02-0412-2
    - EPAMW01-0412
    - EPAMW01d-0412
    - EPAMW01-0412-4
    - EPAMW01-0412-7
    - EPAMW01-0412-10
    - Field Blank 3
    - Field Blank 4
    - Equipment Blank 3
    - Equipment Blank 4

- EPAMW01-0412: Phenol, Matrix spike hi, flag K1 (just this sample as others in batch are from DW wells)

- Calibration criteria not met for Benzo(g,h,i)perylene for batch 1200240, flag J1, some samples flagged, others needing flagged are:
    - PGDW50-0412
    - EPAMW01-0412
    - EPAMW01d-0412
    - Field Blank 3
    - Field Blank 4
    - Equipment Blank 3
    - Equipment Blank 4

- EPAMW01-0412-4, Benzoic acid, flag with J2, outside calibration range

5. VOC-R8:

- Remove U1 flag from 1,2,4-trimethylbenzene for EPAMW02-0412-1 and EPAMW02-0412-2
- Remove U1 flag from Acetone for EPAMW02-0412-1

6. LV-Ethoxy

- Nonylphenol Ethoxylate
    - PGDW20d-0412 should read "0.06" not "0.08"
    - EB4 should read "0.16" not "0.09"

- Nonylphenol
    - EPAMW02-0412-2 should read "7.4-7.9" not "7.4-7.5"

- Octylphenol
    - EPAMW02-0412-7, round "0.098" to "0.10" to be consistent with rest of results

8/26/12 - Regarding Spreadsheet Issues for Metals by ICP-OES

1. The following elements analyzed by ICP-OES have a J2 qualifier in the QC column corresponding to instances for which the total metals analysis was not applicable: Ba, Na, S, and Si. J2 should be removed where the result column says NA.

2. Phosphorus should all have a K3 added for the ICP-OES analysis unless you have information that would prove that all potential interference would be positive.

3. ICP-OES results for Cd, Cr, Cu, Ni, Pb, Se and Tl should be removed since they are being reported by ICP-MS.

4. The pre-digestion matrix spike for Si had 136% recovery for the dissolved and 130% for the total analysis, but Shaw's report narrative does not mention this. All of the results for Si that are >QL should have the K1 data qualifier applied. (Don't forget to add this issue to the QAQC narrative in Appendix B.)

5. There are some L2s showing up in the QC column for Total Ag in the spreadsheet. They should be J2.

6. The J2 qualifier should be applied to all of the results for Total Al. A couple of the high results do not have any data qualifiers.

7. There are a few minor transcription errors or issues with significant figures in the spreadsheet:

   The QL for dissolved Ag should be 14 (not 16).

   The QL for dissolved Ca should be 0.287.

   The QL for total Ca should be 0.319.

   The MDL for dissolved Mg should be 0.030.

   The QL for dissolved Mg should be 0.100.

   The QL for total Mg should be 0.111.

   The numbers for dissolved and total Sr have been rounded-off.

8. The ADQ for this project recommended that all of the total metals results have the J2 qualifier applied because RSKSOP179 is not equivalent in all ways to EPA Method 3015A. While it is agreed that EPA methods are intended to provide guidance, as opposed to requirements, for analytical techniques, the data qualifiers need to be applied for transparency in the process when method deviations could imply to some stakeholders that the method was biased in a certain direction or if there are concerns that the same results would not be reproducible in another lab operating under the same EPA Method. For high visibility ORD QA Category 1 projects, it would be prudent to apply data qualifiers if there are any procedural deficiencies and explain all potential impacts to data quality in the appropriate QAQC sections of the report. The QAQC section of the report is also the most appropriate place to point out all of the evidence that there is to support the level of confidence you feel others should have in the data. Even if the decision is made not to flag the total metals data, you may find this information useful to add to the QAQC discussion in Appendix B for full transparency.

   Below, I have provided some suggested language that you could use as a starting point to describe all of the facts surrounding this issue. It has been written as a comprehensive treatment of the issues surrounding the ICP-OES data quality in the format of the QAQC narrative from Table B30 in the current version of Appendix B.

Suggested "QC Narrative" for Table B30 for ICP-OES: (Of course, this is too long for the table, but this was the easiest way to break out the details here. You might summarize this in the table and include the details elsewhere in Appendix B. You might also decide to indicate the level of importance of certain analytes to this study to indicate whether there is any potential impact to decision-making, or not.)

Dissolved

ICP-OES (filtered/dissolved analysis): A Performance Evaluation (PE) sample was analyzed for K in the same sample set. PE result met acceptance criteria (measured value = 25.6 mg K/L; certified value 26.6 mg/L; acceptance limits = 21.9 - 31.7 mg/L).

The ICP-OES dissolved metals analysis of filtered samples took place over two analytical runs. For both analytical runs, the analytes Ag, Al, B, Ba, K, Na, P, S, and Si had fewer calibration checks analyzed than the method required. These analytes were not included in the QC standard that was designated as the initial calibration verification (ICV) check. However, the analytes were included in a QA standard designated as a second source standard that was analyzed right after the calibration standards and prior to analysis of any other QC checks or any samples. The percent recoveries of all analytes in the second source standard for both runs were acceptable according to the QA criteria of 90 – 110% of known value. The percent recoveries for the nine analytes in question ranged from 93.6 – 103% recovery, indicating that the analytical method was in control for these analytes at the beginning of the sample analyses. For the first run, twenty-four samples were analyzed, and then CCVs for the nine analytes in question were analyzed at the end of the sample analysis. The percent recoveries for these nine analytes in the ending CCVs ranged from 91.5 – 101% recovery, indicating that the analytical method was in control for these analytes at the end of the sample analysis. For the second run, eleven samples were analyzed, and then CCVs for the nine analytes in question were analyzed at the end of the sample analysis. The percent recoveries for these nine analytes in the ending CCVs ranged from 93.6 – 99.3% recovery, indicating that the analytical method was in control for these analytes at the end of the sample analysis. Other factors that indicate that the method was in control for these analytes are as follows: all laboratory blanks were <QL for all analytes, QC checks for analysis of laboratory duplicates were acceptable for all analytes, and matrix spikes were acceptable for all analytes except for Si, which had a high percent recovery, possibly due to the fact that the spiking concentration was too low compared to the concentration found in the spiked sample. Matrix spike recoveries for Na were unable to be calculated for either analytical run because the spiking concentration was less than 20% of the concentration found in the spiked sample. For the first analytical run, the matrix spike for S had an acceptable 85.0% recovery, but for the second analytical run, the matrix spike recovery for S was unable to be calculated because the spiking concentration was less than 20% of the concentration found in the spiked sample. Because analyte concentrations in the sample cannot be known by the analyst ahead of time, and samples to be used for matrix spikes are chosen randomly, being unable to calculate a % recovery because the spike concentration is too low, while unfortunate, is not considered to indicate that method performance was out of control.

Suggested "Impact on Data" for Table B30 for ICP-OES: (I know that the table is written referring to "flagging" data, but I would recommend that the language refer to "data qualifiers" that provide information about the analytical process instead of making them think about the connotation of red flags.)

ICP-OES: Detections below the QL have the J0 data qualifier applied. All of the dissolved metals results for Ag, Al, B, Ba, K, Na, P, S, and Si have the J2 data qualifier applied due to incomplete calibration check frequency. All of the dissolved metals results for Si have the K1 data qualifier applied due to high % recovery in a matrix spike.

Total

The analytes Ag, Al, B, Ba, K, Na, P, S, and Si had fewer calibration checks analyzed than the method required. These analytes were not included in the QC standard that was designated as the initial calibration verification (ICV) check. However, the analytes were included in a QA standard designated as a second source standard that is analyzed right after the calibration standards and prior to analysis of any other QC checks or any samples. The percent recoveries of all analytes in the second source standard for both runs were acceptable according to the QA criteria of 90 – 110% of known value. The percent recoveries for the nine analytes in question ranged from 94.8 – 103% recovery, indicating that the analytical method was in control for these analytes at the beginning of the sample analyses. Twenty-seven samples were analyzed, and then CCVs for the nine analytes in question were analyzed at the end of the sample analysis. The percent recoveries for these nine analytes in the ending CCVs ranged from 97.0 – 109% recovery, indicating that the analytical method was in control for these analytes at the end of the sample analysis. Other factors that indicate that the method was in control for these analytes are as follows: all laboratory blanks were <QL for all analytes, Duplicate QC checks were acceptable for all analytes, and pre- and post-digestion matrix spikes were acceptable for all analytes except for Ag, Na, S, and Si (further discussed below).

All of the unfiltered samples, plus several QC check samples (described where?) are put through the RSKSOP179 Rev. 3 digestion procedure. RSKSOP179 Rev. 3 is similar to EPA Method 3015A with the following notable deviations: no laboratory control sample (analytes spiked into an appropriate blank matrix) is digested, and the total digestion time is 40 minutes instead of the 20 minutes recommended by EPA Method 3015A. The longer total digestion time has the potential to result in more complete digestion of the sample and, hence, influence the results with a high bias compared to 3015A performed with the standard, shorter digestion time. EPA Methods were promulgated to ensure reproducibility of results between laboratories, and the exact effects on data quality are unknown for the lengthier digestion time.

Laboratories customizing EPA Methods in Standard Operating Procedures (SOPs) that are tailored to their analytical equipment, software, and logistical situation is common practice, and performance-based metrics are used to evaluate whether a given procedure is performing with equivalent data quality output as the EPA Method. In trying to determine if data quality was impacted by the lengthier digestion time, the following facts are noteworthy: the digestion blank was <QL for all analytes, QC checks for analysis of digested laboratory duplicates were acceptable for all analytes, and pre-digestion matrix spikes were acceptable for all analytes except for Ag, Na, and Si. If a laboratory control sample had been digested and analyzed, it could be determined whether the digestion method performance was in control and if there were any matrix effects that could be influencing the results of the pre-digestion matrix spikes. The laboratory report acknowledges that the pre-digestion spike for Ag had a low % recovery because only HNO_3 was used in the digestion procedure. While HCl used in the digestion stabilizes Ag, it was deemed too likely to create additional interference effects in the trace metal analysis by ICP-MS subsequent to analysis of the digestate by ICP-OES. Originally both types of analysis were to be done at Shaw Environmental. The post-digestion matrix spike for Ag had 89.2% recovery, indicating that the instrument was in control, but the digestion method had a very low recovery for Ag. The pre-digestion matrix spike for Si had 130% recovery, and the post-digestion matrix spike for Si had 110% recovery indicating the likelihood of a high bias for Si. Matrix spike recoveries for Na were unable to be calculated for either the pre- or post-digestion matrix spike because the spiking concentration was less than 20% of the concentration found in the spiked sample. Because analyte concentrations in the sample cannot be known by the analyst ahead of time, and samples to be used for matrix spikes are chosen randomly, being unable to calculate a % recovery because the spike concentration is too low, while unfortunate, is not considered to indicate that method performance was out of control. The pre-digestion matrix spike for S had an acceptable 76.6% recovery, and the post-digestion matrix spike for S was unable to be calculated because the spiking concentration was less than 20% of the concentration found in the spiked sample, which would not require additional data qualifiers to be applied to the sample results.

Suggested "Impact on Data" for Table B30 for ICP-OES: (I know that the table is written referring to "flagging" data, but I would recommend that the language refer to "data qualifiers" that provide information about the analytical process instead of making them think about the connotation of red flags.)

ICP-OES: Detections below the QL have the J0 data qualifier applied. All of the total metals results for Ag, Al, B, Ba, K, Na, P, S, and Si have the J2 data qualifier applied due to incomplete calibration check frequency. All of the total metals results for Ag have the K2 data qualifier applied due to low % recovery in a pre-digestion matrix spike. All of the total metals results for Si have the K1 data qualifier applied due to high % recovery in a pre-digestion matrix spike.